HIGH-RESOLUTION OXYGEN K-EDGE STUDY OF $YBa_2Cu_{3-x}Fe_xO_{7+y}$

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INTRODUCTION

Metallic substitution studies have enhanced our understanding of the superconducting and normal state properties of high-T_c superconductors. Substitution of metals in $YBa_2Cu_3O_{7-y}$ (YBCO) usually depresses T_c and has other negative effects on the superconducting properties. The superconducting properties of YBCO depend not only on the oxygen stoichiometry but also on the oxygen ordering. Substitution of Cu can provide a selective tool to investigate the specific effects because depending on the dopant characteristics, the substituted compounds may exhibit modified microstructures without any substantial change in the overall oxygen content. Much work has been done in this direction. Trivalent metal ions like Fe, Co, or Al replace Cu in Cu1 site on the Cu-O chain and depress T_c more slowly than divalent Zn and Ni which replace Cu in Cu2 site in the CuO2 plane [1]. Substitution of Cu by Fe may lead to (i) reduction of T_c, (ii) structural transformation with increasing impurity concentration, (iii) increase in oxygen content accompanied by a rearrangement of oxygen, and (iv) local magnetic ordering. When Cu is replaced by Fe, the oxygen atoms might rearrange themselves in order to provide the most stable Fe site. This modifies the local electronic densities of states. Little is known about the variation of electronic structure due to the substitution. Yang et al. [2] have studied the variation of electronic structure of YBCO upon Fe doping, at the Fe site using x-ray absorption spectroscopy (XAS). In this study we compliment their work by investigating O site using XAS.

EXPERIMENTAL

Polycrystals of $YBa_2Cu_{3-x}Fe_xO_{7+y}$ (YBCFO) with starting x values of 0.01, 0.05 and 0.15 were prepared by standard solid state reaction method. The critical temperatures of these samples were determined by standard four-probe technique, using a constant current source and a Keithly-181 nano voltmeter. X-ray diffraction patterns of the samples were obtained using a Phillips PW1700 automated diffractometer. The analysis is computer assisted so that the interplanar spacing values can be corrected for the instrument error function by analyzing a silicon standard and subsequent phase identification.

X-ray absorption near edge structure (XANES) measurements were performed using Advanced Light Source at Lawrence Berkeley National Laboratory on beamline 9.3.2 [3]. High-resolution XANES spectra were taken in the Ba M and O K absorption edge regions, while the monochromator was set at a resolving power (E/ΔE) of > 7000. The YBCFO poly crystal samples were cooled to about 90 K before scraping them in a vacuum of about $1x10^{-10}$ Torr, in order to minimize oxygen loss from the fresh surface [4]. Since the size of the synchrotron radiation photon beam at the sample was ~1 mm, it was not difficult to align the system to make sure that only the sample was illuminated by the photon beam. XANES measurements were performed using a partial electron yield detector consisting of 40 mm channel plates in the pulse counting mode. I_0 signal from a freshly evaporated gold grid was used for normalization of spectra.

RESULTS AND DISCUSSION

The zero-resistance transition temperatures of the samples were 93, 92 and 71 K for x = 0.01, 0.05 and 0.15 respectively. The XRD patterns confirmed that all three samples have single phase with orthorhombic symmetry. This is consistent with the resistivity measurements that revealed all three samples were superconducting.

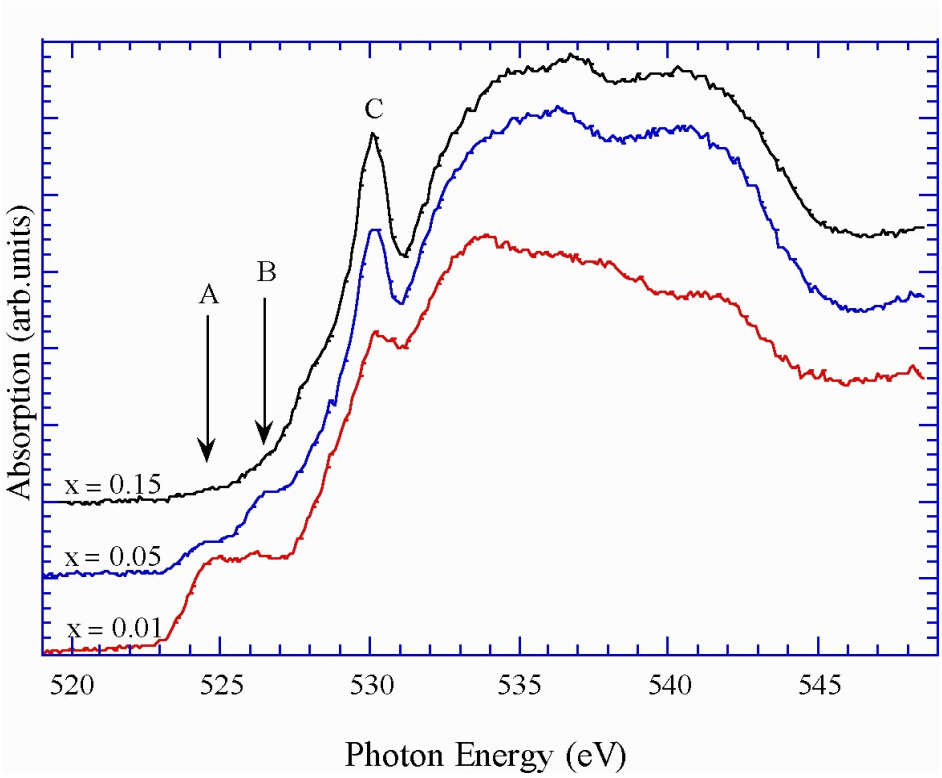

Fig.1: O K edge of $YBa_2Cu_{3-x}Fe_xO_{7+y}$ poly crystals at 90 K as a function of x.

Fig.1 shows the O K edge of YBCFO poly crystals at 90 K as a function of x. Energy scale was corrected by comparing Ba M edge of the samples with that of $YBa_2Cu_3O_{7-y}$ single crystal [5], with the assumption that the Fe substitution does not affect Ba site. A straight line fitted to the region before the peaks (below 523 eV) has been subtracted as background. The spectra shown in the figures have not been smoothed or filtered in any way. Two small peaks at 524.5 and 526.5 eV (labeled A and B respectively) and a prominent peak at 530 eV (labeled C) precede the main edge which starts at about 531 eV. Multiple scattering calculations assign peak A and B to holes in O sites in the CuO2 plane (O2 and O3) and Cu-O chain (O1) respectively [5]. Intensity of peaks A and B decreases with increasing Fe content, indicating hole filling in both CuO2 plane and Cu-O chain. This is in agreement with the recent results from Mossbauer Spectroscopy and neutron diffraction [6,7]. Furthermore, this seems to support that T_c degradation with increasing iron substitution is due to hole filling. In other words, Fe enters the structure primarily in the formally trivalent oxidation state. We interpret the peak C as the signature of the O holes being removed and localized around the Fe sites in the compound. Note that the intensity of this peak increases with increasing Fe content. Our interpretation is further supported by the general observation that many of the insulating transition metal oxides exhibit such sharp peaks between 529 and 530 eV in the O K edge spectra [8].

CONCLUSION

In summary, our high-resolution XANES spectra at O K edge in $YBa_2Cu_{3-x}Fe_xO_{7+y}$ for x = 0.01, 0.05 and 0.15 show hole filling with increasing Fe content in both CuO2 plane and Cu-O chain. This means that Fe enters the structure primarily in the formally trivalent oxidation state. A detailed study of this work including Cu L_3 and Fe $L_{2,3}$ edge regions will be published in the near future.

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